

# Radiation Swelling of Concentrated Alloys<sup>1</sup>

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**Abstract – Irradiation of concentrated alloys is accompanied by the formation of pores, as well as the stratification of solid solutions. These processes occur simultaneously and significantly affect each other. A mathematical model of phase transformations in binary concentrated alloys under the effect of irradiation is proposed. The model is based on the method of thermodynamic analysis. Flows of atoms and vacancies caused by gradients of the corresponding chemical potentials are calculated. The chemical potentials are defined based on volume densities of the energy of interatom bonds, configuration entropy, and elastic energy. The mutual character of diffusion is taken into account. Conditions for the processes of pore formation and element segregation are obtained. The mutual effects of pore formation and alloy element segregation are discussed. A comparison with experimental results is conducted.**

## 1. Introduction

The two most significant effects of irradiation of metallic systems by fast electrons, neutrons, or ions are the formation of radiation pores and the shift in the temperature boundaries of solid solution stability. The authors have earlier studied the formation of pores in pure metals [1, 2], and changes in stability of a solid solution under irradiation [3, 4]. The processes of pore formation and decay of a solid solution occur simultaneously, and therefore they must be described within a unified framework. A model of phase and pore formation in a binary alloy under the effect of radiation is presented in this work. The model is based on thermodynamic analysis. A mechanism of the effect of elastic strains on the oscillation component of entropy is proposed.

## 2. The plan of thermodynamic analysis

The method is based on the assumption that even when metal systems are subjected to such an extreme influencing factor as radiation, the rule of the existence of a local equilibrium is valid. From this follows the possibility of calculating the local densities of the fundamental thermodynamic properties. Knowing the correlation of the local density of Gibbs energy with concentrations, temperature, density, it is possible

to calculate the local values of chemical potentials for atoms of a specific type in an alloy, as well as for quasiparticles (vacancies, interstitial particles). The flows of particles of a specific type are determined by the gradients of the corresponding chemical potentials

$$J_i = -\frac{D_i n_i}{kT} \text{grad } \mu_{xi}. \quad (1)$$

Here  $D_i$  is the diffusion coefficient for particles of a specific type. As a result of transforming the equations for particle flows can be brought to the following form:

$$J_i = -D_{efi} \text{grad } n_i. \quad (2)$$

The equations for the flows in form (2) are suitable for thermodynamic analysis. If there is an area of concentrations and temperatures in which the effective diffusion coefficient for atoms of a specific type assumes negative values  $D_{efi} \leq 0$ , this means that ascending diffusion is occurring. In ascending diffusion, small fluctuations of atoms will grow, which leads to the segregation of alloy elements. In the case of a positive value of the diffusion coefficient (normal diffusion) the alloy preserves its state (does not become stratified). So, if the flows are written for a homogeneous solid solution (even if a hypothetical one), then the positivity of the effective diffusion coefficient demonstrates the fact of the synthesis of a homogeneous solid solution under these conditions.

Similarly the flow of point defects – vacancies can be written. In a vacancy character of diffusion, the flow of vacancies is determined by the sum of flows of atoms of all components of the alloy. The sign of the effective diffusion coefficient of vacancies can indicate whether processes of pore formation will occur in a given metal system. Such processes really occur either when significant strains are applied, or under the effect of radiation.

The mutual character of diffusion processes in a multi-component system is accounted for in the framework of the Darken theory. According to this theory, the flows of atoms in a frame of reference bound to a crystal that is moving with speed  $V$ , equal to:

$$J'_i = J_i - n_i V = J_i - \frac{n_i}{n_0} \sum_i J_i, \quad (3)$$

here  $n_0$  is the concentration of crystal lattice nodes.

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The method of analysis of atom flows described above is quite informative, as it leads to the condition of stratification. It is convenient to use this method in calculating the shift of temperature and concentration stability boundaries of specific phases when external influences are applied to the material. Although in many cases stratification in a metal system leads to processes of self-organization [5], which manifests itself in the appearance of spatial periodic structures. The small perturbation method is used for determining the spatial scale of stratification. If there is a certain stationary solution for concentration of atoms of a specific type, then a small linearized perturbation is added to this solution:

$$n_i(\vec{r}, t) = n_{0i} + \delta n \exp(-i\omega t - i\vec{k}\vec{r}). \quad (4)$$

Substituting solutions (4) into the equations of continuity produces equations for stationary values and their perturbations. Such a simplified approach can be justified by the more stringent Laplace's method. The system of continuity equations becomes algebraic. By equating its determinant to zero, it's possible to find the relationship between the wave vector (real) and frequency (imaginary) – dispersion equation. Assuming that the maximum increment of growth belongs to the mode with wave number  $k_{\max}$ , for which the absolute value  $|\omega|$  assumes the maximum value. This particular mode will determine the solution, which basically is the fact of growth of random fluctuations of concentration of atoms. Further, the spatial scale of the emerging instability is determined:

$$\lambda = \frac{2\pi}{k_{\max}}. \quad (5)$$

The standard calculation of configuration entropy density is linked in statistical mechanics with counting the number of ways that atoms can be exchanged between nodes of the crystal lattice. Although in the case of a multicomponent alloy, the direct statistical approach becomes too cumbersome. At present, the method of quasi-chemical analogy is used for researching reactions with defects [6, 7]. The foundation of this method is that the same approach is used for reactions with defects, their description and explanation, as the approach used for normal chemical reactions. With this purpose, structural elements of the lattice, as well as its unoccupied nodes (vacancies) and interstitials, are considered to be individual objects that can participate in a chemical interaction.

In the case of an alloy consisting of  $m$  different types of atoms, the entropy contribution into the chemical potential of atoms of type  $i$  is determined by the condition:

$$\Delta\mu_{si} = -kT \ln \frac{n_i}{n_v}. \quad (6)$$

Accordingly, the entropy contribution into the chemical potential of vacancies equals

$$\Delta\mu_{sv} = -kT \left( m \ln n_v - \ln \prod_1^m n_i \right). \quad (7)$$

A simple model, in which only the bonding energies of each atom with its nearest neighbors are considered, is accepted for calculating the internal energy.

### 3. Internal strains

The influence of radiation leads to significant concentrations of excess vacancies within the volume of metal material, which is equivalent to the effect of elastic stretching strains, as the distances between atoms grow. So, all structure-phase transformations in alloys under irradiation have to be described within the model of a material undergoing high negative pressures.

A point defect in a lattice of any type in the model of elastic continuum is considered as a point source of deformations and strains in the elastic medium. If there is not one but  $n$  defects that are placed at the points characterized by radius-vectors  $r_m$ , then the resulting shift of a limitless medium in a point characterized by radius-vector  $r$ , is defined by the formula

$$U_1(r) = \sum_{m=1}^n A \frac{r - r_m}{|r - r_m|^3}. \quad (8)$$

In a limited body, in a general case for a body of any shape, the shifts caused by image forces cannot be traced in detail even for a single defect. So, in the presence of  $n$  defects we can only say that the resulting shift  $U_2(r)$  that is linked to these forces will be a gradually changing function of coordinates at distances of the magnitude of several sizes of the body. It's possible to show that in the case when defects are distributed in a randomly shaped body chaotically and on average homogeneously, and the linear dimensions of the body significantly exceed the average distance between defects, the body undergoes homogeneous expansion (or contraction) without changing its shape (not considering its small localized distortions next to the defects).

A fact that appears important is that when excess vacancies, approximately homogeneously distributed throughout the volume of a sample of a crystal, elastic stretching strains appear, with their magnitude proportional to the concentration of vacancies

$$\sigma = -Bn_v. \quad (9)$$

Here coefficient  $B$  depends on the power of the defect, the elastic properties of the medium, the shape and the size of the sample.

### 4. Contribution of elastic strains into the thermodynamic functions

Consider a binary alloy subjected to an external uniform pressure that does not cause plastic deformation.

In order to describe atom oscillations in multi-component alloys, it is convenient to use the notion of an ensemble of harmonic oscillators – oscillations of two neighboring atoms relative to the common mass center. In a binary alloy, there are three such ensembles, associated with oscillations of pairs A–A, B–B, and A–B. When singling out a specific oscillator (pair of atoms) it's necessary to consider the additional oscillating forces from the neighboring atoms. The Schrödinger equation yields identical solutions for the cases of potential energies

$$U = \frac{kx^2}{2} \quad \text{and} \quad U = \frac{kx^2}{2} \left[ 1 + \delta \exp(i\omega t) \right]$$

for any  $\omega$ . It is possible to build the statistical sums for three canonical ensembles and to determine the density of free energy for heat oscillations of atoms. The simplest expression of free energy is in the Einstein approximation:

$$U = U_0 + kT \sum n_{ij} \ln \left[ 1 - \exp \left( -\frac{h\nu_{ij}}{kT} \right) \right]. \quad (10)$$

In order to link external pressure and free energy of atom oscillations, it is convenient to utilize Grüneisen equation

$$\frac{\partial(\ln \nu)}{\partial(\ln V)} = -\gamma,$$

where  $\gamma$  is the Grüneisen parameter. The equation above links the change in atom oscillation frequency to the change in volume, which in its turn is defined by the pressure

$$\frac{1}{K} = - \left( \frac{\partial V}{\partial P} \right)_T,$$

where  $K$  is the modulus of uniform pressure. This results in

$$\ln \left( \frac{\nu}{\nu_0} \right) = \frac{\gamma}{K} P = \frac{3\gamma(1-2\sigma)}{E} P = bP. \quad (11)$$

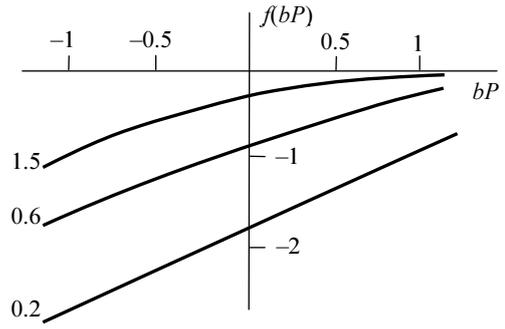
Here  $E$  is the elastic modulus;  $\sigma$  is the Poisson's ratio. Value  $b$  characterizes bonds of a specific type. So,  $b_{aa}$ ,  $b_{bb}$  are calculated based on properties of pure metals. In first approximation we can use

$$b_{ab} \approx b_{aa} \frac{n_a}{n_0} + b_{bb} \frac{n_b}{n_0}.$$

Next it is useful to consider the function

$$f(bP) = \ln \left\{ 1 - \exp \left[ -\frac{h\nu_0}{kT} \exp(bP) \right] \right\}.$$

The figure represents the calculated dependencies  $f(bP)$  for variable parameters  $x_0 = h\nu_0/kT$ .



Function  $f(bP)$ . The numbers next to the curves correspond to the value of parameter  $x_0$

It is clear from the graph that for lower pressures the dependency  $f(bP)$  is practically linear. The same conclusion follows from decomposition

$$f(bP) \approx \ln \frac{h\nu_0}{kT} + bP.$$

The change in free energy under pressure has the following form:

$$\Delta A = A(P) - A(0) = kT (n_{aa} b_{aa} + n_{bb} b_{bb} + n_{ab} b_{ab}) \cdot P. \quad (12)$$

The contributions into chemical potentials conditioned by external pressure are determined by the equations:

$$\Delta \mu_{xa}^* = \frac{zkT}{n_0} n_a bP + \text{const};$$

$$\Delta \mu_{xb}^* = \frac{zkT}{n_0} n_b bP + \text{const}. \quad (13)$$

### 5. Conditions of instability of a binary array under irradiation

Chemical potentials of atoms of different types, written with the consideration of density of inter-atom bond energy, configuration entropy, and elastic strains, have the following form:

$$\mu_{xa} = kT (\ln n_a - \ln n_v) + \frac{n_a z \Delta \varepsilon}{n_0} - \frac{n_a}{n_0} kT z \Delta b B n_v - z \Omega B n_v;$$

$$\mu_{xb} = kT (\ln n_b - \ln n_v) + \frac{n_b z \Delta \varepsilon}{n_0} -$$

$$- \frac{n_b}{n_0} kT z \Delta b B n_v - z \Omega B n_v. \quad (14)$$

Here  $z$  is the coordination number;  $\Delta \varepsilon = \varepsilon_{aa} + \varepsilon_{bb} - 2\varepsilon_{ab}$  ( $\varepsilon_{ij}$  is the energy of the corresponding inter-atom bond),  $\Delta b = b_{aa} + b_{bb} - 2b_{ab}$ . The movement of atoms through nodes of a crystal lattice is defined by diffusion coefficient  $D'$ . Equilibrium diffusion coefficient in the absence of external influencing factors is expressed via the vacancy formation energy and the migration energy  $E_m$  of an atom. Under the effect of radiation,

quasi-equilibrium excess vacancies are generated with concentrations  $n_v$ , defined by the pattern of radiation, temperature, state of the sinks. Besides this, it is necessary to account for the influence of elastic strains on the frequency of jumps of an atom between lattice nodes. This results in

$$D' = \frac{n_v}{n_0} D = \frac{n_v}{n_0} D_0 \exp\left(-\frac{E_m + \sigma\Omega}{kT}\right). \quad (15)$$

Atom flows caused by gradients of chemical potentials are expressed in the form

$$J_i = -D_i \frac{n_i}{n_0} \left[ 1 - \frac{n_i}{n_0} \left( \frac{z\Delta\varepsilon}{kT} + z\Delta b\sigma \right) \right] \nabla n_i + D_i \frac{n_i}{n_0} \left( 1 - z \frac{n_i}{n_0} \Delta b\sigma + \frac{\sigma\Omega}{kT} \right) \nabla n_v. \quad (16)$$

Equations (16) demonstrate that the movement of atoms of a specific type is caused by the gradient of concentration of these atoms, as well as the gradient of concentration of vacancies. In order to obtain the condition of stability of a solid binary solution as it relates to stratification (segregation of elements) it is necessary to take into account the mutual character of diffusion within the framework of Darken theory. Flows of atoms in the frame of reference bound to the moving surfaces of a crystal lattice are equal to

$$J'_a = -\tilde{D} \frac{n_v}{n_0} \left[ 1 - \frac{(D_a + D_b)n_a n_b}{\tilde{D} n_0^2} \left( \frac{z\Delta\varepsilon}{kT} + z\Delta b\sigma \right) \right] \nabla n_a. \quad (17)$$

Here  $\tilde{D} = (D_a n_b + D_b n_a) / n_0$  is mutual diffusion coefficient. The condition of stratification in a binary system has the form

$$\frac{n_a n_b}{n_0^2} \left( \frac{z\Delta\varepsilon}{kT} + z\Delta b\sigma \right) \geq \frac{\tilde{D}}{(D_a + D_b)}. \quad (18)$$

To obtain the conditions of destabilization of an alloy as it relates to the formation of radiation pores, equations (16) need to be used, with flow of vacancies expressed as  $J_v = -(J_a + J_b)$ , which includes the portions of the flows of atoms that contain the vacancy concentration gradient:

$$J_v = -\frac{n_v}{n_0} \left[ D_1 \left( 1 + \frac{\sigma\Omega}{kT} \right) + D_2 z \Delta b\sigma \right]. \quad (19)$$

The following substitutions are used here:

$$D_1 = \frac{D_a n_a + D_b n_b}{n_0}, \quad D_2 = \frac{D_a n_a^2 + D_b n_b^2}{n_0^2}.$$

The condition of the formation of radiation pores in an alloy has the form

$$\frac{\sigma\Omega}{kT} - \frac{D_2}{D_1} z \Delta b\sigma \geq 1. \quad (20)$$

## 6. Conclusion

Stratification and pore formation are caused by different factors. In this regard, the two described phenomena have a relatively weak relation to one another, although in each case there exists an influence of the energy of atom oscillations.

The proposed phenomenological theory of the influence of radiation on alloys allows us to qualitatively explain the observed phenomena of radiation swelling and the separation of new phases in unsaturated solutions. Detailed calculations for specific solutions are being conducted.

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